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The photooxidation of formaldehyde with sunlamps ($E_{max} \approx 3100$ Å) produces hydrogen peroxide (H_2O_2) at varying concentrations depending upon the amount of water vapor present. It is postulated that the variable production of H_2O_2 is a result of condensation on the reactor surface. Rainwater samples were also analyzed for H_2O_2. Summer rain in the Research Triangle area of North Carolina contained as much as 200 ppb (w/w) of H_2O_2. Contrastingly, rainwater collected in December contained much less H_2O_2, usually 2-8 ppb. The lower concentrations found in the colder conditions is attributed to a decrease in photochemical activity.

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HYDROGEN PEROXIDE FORMATION FROM THE PHOTOOXIDATION OF FORMALDEHYDE AND ITS PRESENCE IN RAINWATER

J. J. Bufalini, H. T. Lancaster, G. R. Namie, and B. W. Gay, Jr.

Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ABSTRACT

The photooxidation of formaldehyde with sunlamps (E_{max} ≈ 3100 Å) produces hydrogen peroxide at varying concentrations depending upon the amount of water vapor present. It is postulated that the variable production of H_2O_2 is a result of condensation on the reactor surface. Rainwater samples were also analyzed for H_2O_2. Summer rain in the Triangle area of North Carolina contained as much as 200 ppb (w/w) of H_2O_2. Rainwater collected in December contained much less H_2O_2, usually 2-8 ppb. The lower concentration found in the colder conditions is attributed to a decrease in photochemical activity.

INTRODUCTION

Hydrogen peroxide (H_2O_2) is produced in the photooxidation of formaldehyde[1,2] and it has been detected in polluted atmospheres.[3] In these earlier studies, the production of H_2O_2 was measured with a difficult colorimetric method which required a large sample and extreme experimental care[4].

In an attempt to verify the earlier measured levels of hydrogen peroxide produced from the photooxidation of formaldehyde using a more sensitive H_2O_2 measurement technique[5], it was found that the H_2O_2 concentrations were much lower than previously re-

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ported. The observed difference in H_2O_2 yield could not be explained by employment of the new measurement technique.

This note reports the results from a set of experiments which were undertaken to explain this difference. The findings led us to suspect that rainwater should contain measurable levels of H_2O_2. The confirmation of H_2O_2 in rainwater is important in the heterogeneous oxidation of sulfur dioxide in the atmosphere.

EXPERIMENTAL

The experimental system used for the photooxidation experiments is similar to that reported earlier[1]. However, sixteen (FS-40) sunlamps were used in this study compared with the 28 sunlamps used earlier. The light intensity was not measured in this study but should be approximately 4/7 of that employed in the earlier work since light intensity is almost proportional to the number of lights used in the chamber. The light intensity in the earlier study[1] was measured by the initial rate of disappearance of nitrogen dioxide in an inert atmosphere (nitrogen) and was found to be 0.14 min^{-1} with 28 sunlamps.

The formaldehyde samples were irradiated in a 160 liter Teflon bag. These formaldehyde samples were prepared by heating a known quantity of α-polyoxymethylene in an air stream to the 160 liter bag. The formaldehyde was measured by chromotropic colorimetric method[6].

The hydrogen peroxide was measured by the new chemiluminescent technique based on the oxidation of 5-amino-2,3-dihydro-1,4-phthalazinedione (luminol) by H_2O_2 in the presence of a Cu(11) catalyst[5].

The air employed in this study was ambient outside air that was catalytically purified by combustion when passed through a heated catalyst and filtered through activated charcoal and Purafil. After purification, the air contained less than 2 ppb NMHC (non methane hydrocarbon) and less than 1 ppb of NO_x. The

relative humidity of the ambient air was not measured. However, it is probable that the humidity was very high since the outside temperature was quite high (~ 33°C). Upon cooling to room temperature of ~ 26°C, the relative humidity is probably close to 100%.

The average temperature within the chamber was controlled to 25 ± 2°C with an air conditioner in back of the irradiation chamber. However, there were bag surface temperature gradients of 6°C, coldest near the cold air discharge at the back of the chamber. This temperature gradient and the chamber relative humidity appear to be important factors that differ from the earlier study.

RESULTS AND DISCUSSION

The data obtained from the photooxidation of formaldehyde under wet and dry conditions are shown in Figure 1. There is a striking difference in the H_2O_2 curves under the two different conditions.

In Table 1 are shown the results from the most recent experiments as well as the data from the earlier study. The ratio of H_2O_2/aldehyde is much lower in this study at 25°C. Although

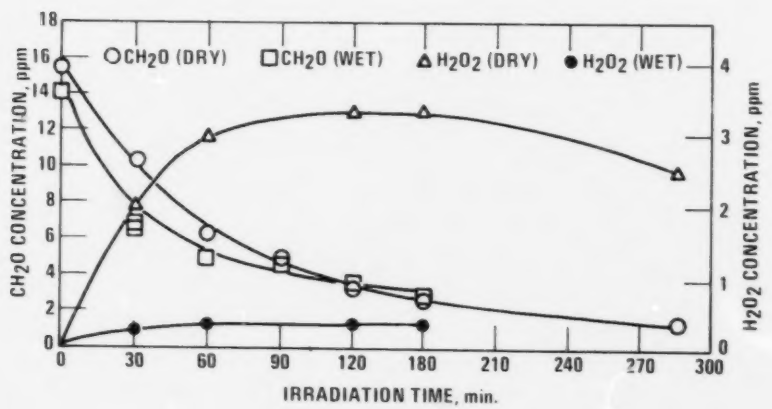

Figure 1

Hydrogen peroxide formation in photo oxidation of formaldehyde under wet and dry conditions.

TABLE 1

Ratio of Hydrogen Peroxide Formed to Formaldehyde Reacted Under Humid and Dry Conditions

Irradiation Time (min.)	$[H_2O_2]/[HCHO]_{reacted}$			
	25°C[a]	50°C[a]	25°C(dry)[a]	23°C[b]
30	0.041	0.405	0.385	0.052
60	0.035	0.400	0.337	0.115
120	0.031	0.375	0.280	0.127
180	0.029	0.298	0.220	0.090
240	-	-	0.220	0.090

[a] Formaldehyde initially 14 ppm

[b] Data from earlier study CH_2O initially 12.5 ppm (1)

the light intensity in the new data was lower, the amount of H_2O_2 formed per formaldehyde reacted should not be greatly different from the earlier study. It was observed that water vapor condensed on the inner surface of the bag in the area closest to the air conditioner when the air conditioner was operating. Therefore, it was suspected that H_2O_2 may be irreversibly adsorbed on the bag surface during the water condensation process.

To test the adsorption process, two additional experiments were conducted; the first at 50°C and the second at 25°C but with dry tank air. Data in Table 1 show that the higher temperature (50°C) produces more H_2O_2. Similar results were obtained with dry tank air (25°C dry). These two experiments suggest the hypothesis is valid since more H_2O_2 was observed in both cases. Theory predicts that high temperatures would degrade H_2O_2 more quickly while a higher water vapor concentration should increase H_2O_2 formation[7]. The two experiments showed opposite effects

i.e. more H_2O_2 was produced at the higher temperature and also at lower humidity.

The dry experiments produced more H_2O_2 than the earlier experiments. It is not immediately obvious why the recent experiments show more H_2O_2. Perhaps the total water vapor in the system has some effect on the amount of H_2O_2 detected. The earlier experiments may also have had considerable water vapor present but not sufficient to cause noticeable condensation. Relative humidity measurements were not made in the earlier study.

Having established that gas phase H_2O_2 easily condenses with water vapor, rainwater, samples were analyzed for H_2O_2 since it was reported that H_2O_2 is extremely soluble in cloud droplets[8]. Rainwater samples were collected on June 8-9, June 22, July 11, August 19-20, and December 5, 1978. Snowfall samples were collected on January 31, 1979. All the June and July samples showed H_2O_2 concentrations between 100-200 ppb (wt/wt). The August samples varied between 40-50 ppb while the December samples contained only 2-8 ppb. The snowfall samples contained even lower concentrations of H_2O_2-the average concentration being approximately 0.5 ppb. The data suggest that with decreasing temperatures and photochemical activity the amount of H_2O_2 also decreases. If washout were the dominant mechanism for H_2O_2 removal, then more H_2O_2 would be observed early in the rain. However, if rain-out (adsorption by cloud elements) were the main removal route, then a relatively constant level of H_2O_2 would be observed during the rain period. The samples of rainwater varied dissimilarly and no particular pattern could be established for the H_2O_2 concentrations with respect to a time period during the rain. In the August 19 rain, the H_2O_2 concentration in collected rain samples increased from 12 ppb at 1606, 40 ppb at 1618, 43 ppb at 1630, and to 50 ppb at 1638 hours EST. At 1654 hours the H_2O_2 was at a low of 4 ppb. In many cases, the rainwater was dirty i.e., the collected rain samples contained a large quantity of black solid matter. There is the possibility that there are two factors opposing one another;

early in the rain, the H_2O_2 concentration initially is high but because of the associated high solid matter also observed in the early rain, some H_2O_2 is destroyed. Later in the rain, the H_2O_2 concentration would be less but because the solid material is also less, H_2O_2 persists and is observed at equally high or even higher concentration than early in the storm. Also, the history of the rain is important depending upon the trajectory of the air mass. The amount of H_2O_2 which accumulates in precipitation clouds may vary widely.

To make certain that H_2O_2 was properly identified, i.e., that some other compound is not giving a positive H_2O_2 signal on the H_2O_2 instrument, MnO_2 was added to the rainwater samples. In all cases, the response signal decreased over 95%. The addition of MnO_2 to H_2O_2 samples had been previously tested in the laboratory. In all samples H_2O_2 was destroyed with the addition of MnO_2. Ozone if dissolved in rainwater would not respond to the luminol reagent.

It is interesting to note that if these measurements of H_2O_2 in rainwater are correct, then the heterogeneous reaction of H_2O_2 in rainwater or liquid aerosol with SO_2 could be a significant oxidation process for SO_2 in the atmosphere as suggested by others[8].

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